

#### CERTIFICATE

l, Shingo NISHIDE, a patent attorney of TOKOSHIE PATENT FIRM of Hoshino Dai-ichi Bldg., 8-3, Nishishinjuku 8-chome, Shinjuku-ku, Tokyo, Japan hereby certify that to the best of my knowledge and belief the following is a true translation into English of the accompanying Japanese Patent Application Serial No.2004-109870 in the name of Sumitomo Mitsubishi Silicon Corporation (SUMCO Corporation).

Signed this 29th day of July, 2010

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## <Name of Document> CLAIMS

- <Claim 1> An alkali etchant for controlling surface roughness of a semiconductor wafer, which is a sodium hydroxide solution having a weight concentration of 55 wt% to 70 wt%.
- <Claim 2> The alkali etchant for controlling surface roughness of a semiconductor wafer as set forth in claim 1, wherein a temperature of the solution is 80°C to 90°C when weight concentration of said sodium hydroxide solution is 60 wt% to 70 wt%, and a temperature of the solution is 85°C to 90°C when weight concentration of said sodium hydroxide solution is 55 wt% to 60 wt%.
- <Claim 3> A production method of a semiconductor wafer comprising the step of etching a main surface of a both-side mirror finished semiconductor wafer by bringing the main surface contact with a sodium hydroxide solution, wherein a temperature is 80°C to 90°C and weight concentration is 60 wt% to 70 wt%, or a sodium hydroxide solution, wherein a temperature is 85°C to 90°C and weight concentration is 55 wt% to 60 wt%.
- <Claim 4> The production method of a semiconductor wafer as set forth in claim 3, furthermore comprising the step of neutralizing by an acid solution the main surface of the wafer contacted with said etchant after said etching step.
- <Claim 5> The production method of a semiconductor wafer as set forth in claim 4, wherein said acid solution contains ozone.
- <Claim 6> The production method of a semiconductor wafer as set forth in claim 4, wherein a wafer surface is processed by using an ozone solution after the neutralizing step by said acid solution.

<Name of Document> DESCRIPTION

<Name of invention> ALKALI ETCHANT FOR CONTROLLING SURFACE ROUGHNESS OF SEMICONDUCTOR WAFER

#### <TECHNICAL FIELD>

[0001] The present invention relates to an etchant (etching solution) for controlling surface roughness of a semiconductor wafer, and particularly relates to an etchant capable of suppressing deterioration of global flatness of a semiconductor wafer to lower the gloss level.

<BACKGOUND ART>
[0002]

Chemical etching of a silicon wafer is performed for removing a damage layer (alteration layer due to processing) on a surface of the silicon wafer caused mainly by a mechanical processing step, such as block cutting, outer layer grinding, slicing and wrapping, and is also performed on the back surface in some cases, so that front and back of a silicon wafer, wherein both sides are mirror polished, can be identified. [0003]

In chemical etching for removing a damage layer, an acid etchant or an alkali etchant is used as the etchant. The former is an etchant formed by three components, wherein mixed acids of fluorinated acid (HF) and nitric acid (HNO<sub>3</sub>) is diluted by water (H<sub>2</sub>O) or by acetic acid (CH<sub>3</sub>COOH). Silicon Si is oxidized by the nitric acid to generate SiO<sub>2</sub>, then, the SiO<sub>2</sub> is dissolved by fluorinated acid and removed. The latter etchant is an etchant obtained by diluting potassium hydroxide (KOH) or caustic soda (NaOH), etc. by water. As a result of such chemical etching, a processing alteration layer of a silicon wafer is removed, so that the surface roughness is reduced and a smooth surface is obtained.

[0004]

However, the conventional etchant as explained above has not been able to uniformly lower the gloss level of a mirror surface of a mirror finished silicon wafer while maintaining a global flatness level, for example, TTV (total thickness variation: a difference (µm) of a maximum value and a minimum value of wafer surface height when fixing the wafer back surface by suction; GBIR of the SEMI standard).

# <DISCROSURE OF THE INVENTION> [0005]

An object of the present invention is to provide an etchant capable of suppressing deterioration of a global flatness level and sufficiently lowering a gloss

level of a wafer, and a production method of a semiconductor wafer.

To attain the above object, according to a first aspect of the present invention, there is provided an alkali etchant for controlling surface roughness of a semiconductor wafer, which is a sodium hydroxide solution having a weight concentration of 55 wt% to 70 wt%.

[0006]

Also, to attain the above object, according to a second aspect of the present invention, there is provided a production method of a semiconductor wafer comprising the step of etching a main surface of a both-side mirror finished semiconductor wafer by bringing the main surface contact with a sodium hydroxide solution, wherein a temperature is 80°C to 90°C and weight concentration is 60 wt% to 70 wt%, or a sodium hydroxide solution, wherein a temperature is 85°C to 90°C and weight concentration is 55 wt% to 60 wt%.

[0007]

In the present invention, a mirror surface of a wafer is etched by using an alkali etchant having an anisotropic etching property, that an etching speed in the depth direction is larger than that in the horizontal direction. Therefore, the etching speed is slow, yet roughness of the surface can be increased, consequently, deterioration of the global flatness level can be suppressed. Furthermore, at this time, the gloss level can be lowered by setting weight concentration of sodium hydroxide or potassium hydroxide to 55 wt% to 70 wt%.

# <BEST MODE FOR CARRYING OUT THE INVENTION> [0008]

Below, an embodiment of the present invention will be explained based on the drawings.

First, to explain a production method of a semiconductor wafer according to the present embodiment with reference to FIG 1(A), in wafer processing of this example, a silicon wafer is produced through steps of slicing, chamfering, etching, mirror polishing, etching (clouding or roughening processing), pure water washing, neutralizing, pure water washing, drying and inspection. Below, the respective steps will be explained in detail.

[0009]

A silicon ingot grown by the CZ method is sliced to, for example, an 8-inch silicon wafer having a thickness of 860µm or so in a slicing step in a step S1. Next, edges of the sliced silicon wafer is chamfered to be a predetermined shape by a

chamfering grind stone in a chamfering step in a step S2. As a result, edges of the silicon wafer are shaped to be rounded as prescribed (for example, a MOS type chamfered shape). Then, the chamfered silicon wafer is wrapped by a wrapping step in a step S3. In the wrapping step, the silicon wafer is placed between a pair of wrapping boards being in parallel with each other, then, a mixture of alumina abrasive grains, and a dispersant and water is poured as a wrapping solution between the wrapping boards, and rotation and rubbing are performed under applying a pressure, so that both of the front and back surfaces of the wafer are mechanically wrapped. At this time, a wrapping amount of the silicon wafer is, for example, 30 to 80µm or so for both of the back and front surfaces of the wafer.

[0010]

Next, in a step S4, the wrapped wafer after the wrapping is etched. Specifically, by immersing the silicon wafer in a mixed acid solution obtained by mixing fluorinated acid and nitric acid (from normal temperature to  $50^{\circ}$ C), etching of, for example,  $20\mu m$  for one surface and  $40\mu m$  or so for both surfaces is performed. As a result, distortion in the wrapping step and distortion in the chamfering step, etc. are removed. [0011]

Next, both surfaces of the silicon wafer are mirror polished in a step S5. This step is performed by using a polishing apparatus having a rotating upper polishing board and a rotating lower polishing board arranged to face to each other. A polishing cloth is attached to each of the upper polishing board and the lower polishing board, and the silicon wafer is pressed against the upper and lower polishing cloth, so that the both surfaces are mirror polished at a time. A polishing allowance at this time is, for example, 10µm. Predetermined slurry is supplied when performing the mirror polishing.

When the mirror polishing finishes, the silicon wafer is taken out from the polishing apparatus and, in a step S6, clouding processing is performed by etching only the back surface of the wafer, wherein both surfaces are mirror finished. At this time, the alkali etchant according to the present invention is used.

[0013]

The alkali etchant according to the present embodiment is for enabling easier identification of front and back with eyes by lowering a gloss level of the back surface of the wafer and has a characteristic of reducing gloss without deteriorating global flatness level of the back surface.

[0014]

As an alkali etchant according to the present embodiment, a solution including

sodium hydroxide NaOH as the main component, wherein weight concentration (volume mole concentration) of sodium hydroxide is 55 wt% (22.3 mol/L) to 70 wt% (31.3 mol/L), may be selected. When the weight concentration of the sodium hydroxide is lower than 55 wt%, etching progresses, but reducing of the gloss is not observed and identification of front and back surfaces with eyes becomes impossible. Also, an etchant including sodium hydroxide having weight concentration of exceeding 70 wt% is not suitable in terms of an etching processing temperature because it does not dissolve unless a temperature of the etchant is heightened to 100°C or so.

[0015]

Note that since solubility of sodium hydroxide to water is 50 wt% or so at a normal temperature, a temperature of the etchant is set to  $80^{\circ}$ C to  $90^{\circ}$ C in the etching step in the step S6, a back surface of the wafer to be subjected to clouding processing is etched, for example, by 20 to  $30\mu m$ . [0016]

In the etching step in the step S6, a potassium hydroxide solution may be also used instead of the sodium hydroxide solution. When using a potassium hydroxide solution, if a potassium hydroxide solution having a volume mole concentration in the same range as that of the volume mole concentration of the sodium hydroxide solution explained above is used, the same etching effect as that obtained by the sodium hydroxide solution is obtained. Note that when comparing a sodium hydroxide solution with a potassium hydroxide solution having the same volume mole concentration, the potassium hydroxide has a larger molecular weight, so that an absolute value in a weight concentration range also becomes large and it becomes harder to obtain a solution thereof. Accordingly, a sodium hydroxide solution is preferably used as an alkali etchant in a point that it is easily made to be a solution.

[0017]

When alkali etching is finished, the wafer is washed by immersing it in pure water or by spraying pure water thereon (pure water washing in a step S7), and neutralizing processing is performed for neutralizing the residual alkali etching solution on the wafer (a step S8). In the neutralization processing, the wafer is immersed in a fluorinated acid solution in a weight concentration of 10 wt% or lower at a normal temperature for 5 minutes. At this time, by adding ozone to the fluorinated acid solution, an oxidization film is formed on the wafer surface. Due to this, the silicon wafer surface is not exposed and it is possible to prevent contamination by metal impurities and adhesion of particles.

[8100]

When the neutralizing processing finishes, the wafer attached with a fluorinated acid solution is washed by immersing it in pure water or spraying pure water thereon (pure water washing in the step S9) and, after that, spin drying, for example, at a rotation speed of 1500 rpm is performed for 120 seconds to dry the wafer (a step S10). [0019]

When the above steps finish, wafer flatness level is inspected in a step S11. In the inspection, for example, a flatness measurement device having a capacitance type distance sensor is used and, for example, wafers having GBIR(TTV) of 1.5µm or less is determined to have a flatness level and those which do not satisfy that are determined to be defective in the flatness level.

[0020]

Note that, in the steps S8 to S10 explained above, ozone was added to the fluorinated acid solution in the step S8 for forming an oxidization film on the wafer surface, however, as shown in a step S8' in FIG. 1(B), a fluorinated acid solution not added with ozone may be used in the neutralizing step and, for example, an ozone solution of 10ppm or more may be sprayed on the wafer immediately before the spin drying in a step S10'.

<EXAMPLES>

[0021]

Below, further detailed examples of the present invention will be explained. [0022]

#### Example 1

While keeping a 51 wt% of sodium hydroxide solution at 90°C, sodium hydroxide flakes having a purity of 99% were added thereto, so that an alkali etchant composed of a sodium hydroxide solution having weight concentration of 70 wt% was fabricated. In the alkali etchant kept at 90°C, one surface of a both-side mirror finished silicon wafer subjected to the processing in the steps S1 to S5 shown in FIG. 1 was immersed until an etching depth (allowance) reaches 30µm. The wafer, wherein one surface was subjected to clouding processing as above, was subjected to pure water washing, neutralizing processing, pure water washing and drying in respective steps of the steps S7 to S10 shown in FIG. 1. As a neutralizing agent in the step S8, a fluorinated acid solution in weight concentration of 10 wt% added with 10ppm of ozone was used and the processing was performed at a room temperature for 5 minutes.

[0023]

#### Example 2

Other than fabricating an alkali etchant composed of a sodium hydroxide solution having weight concentration of 70 wt% by keeping 51 wt% of a sodium hydroxide solution at 85°C and adding sodium hydroxide flakes having a purity of 99% thereto in the example 1, a wafer was processed under the same condition as that in the example 1.

[0024]

#### Example 3

Other than fabricating an alkali etchant composed of a sodium hydroxide solution having weight concentration of 70 wt% by keeping 51 wt% of a sodium hydroxide solution at 80°C and adding sodium hydroxide flakes having a purity of 99% thereto in the example 1, a wafer was processed under the same condition as that in the example 1.

[0025]

#### Example 4

Other than fabricating an alkali etchant composed of a sodium hydroxide solution having weight concentration of 60 wt% by keeping 51 wt% of a sodium hydroxide solution at 90°C and adding sodium hydroxide flakes having a purity of 99% thereto in the example 1, a wafer was processed under the same condition as that in the example 1.

[0026]

## Example 5

Other than fabricating an alkali etchant composed of a sodium hydroxide solution having weight concentration of 60 wt% by keeping 51 wt% of a sodium hydroxide solution at 85°C and adding sodium hydroxide flakes having a purity of 99% thereto, a wafer was subjected to processing under the same condition as that in the example 1.

[0027]

#### Example 6

Other than fabricating an alkali etchant composed of a sodium hydroxide solution having weight concentration of 60 wt% by keeping 51 wt% of a sodium hydroxide solution at 80°C and adding sodium hydroxide flakes having a purity of 99% thereto in thee example 1, a wafer was processed under the same condition as that in the example 1.

[0028]

# Example 7

Other than fabricating an alkali etchant composed of a sodium hydroxide

solution having weight concentration of 55 wt% by keeping 51 wt% of a sodium hydroxide solution at 90°C and adding sodium hydroxide flakes having a purity of 99% thereto in the example 1, a wafer was processed under the same condition as that in the example 1.

[0029]

#### Example 8

Other than fabricating an alkali etchant composed of a sodium hydroxide solution having weight concentration of 55 wt% by keeping 51 wt% of a sodium hydroxide solution at 85°C and adding sodium hydroxide flakes having a purity of 99% thereto, a wafer was processed under the same condition as that in the example 1. [0030]

## Comparative Example 1

Other than keeping the alkali etchant composed of 50 wt% of a sodium hydroxide solution at 90°C and using the same for performing clouding processing in the example 1, a wafer was processed under the same condition as that in the example 1. [0031]

# Comparative Example 2

Other than keeping the alkali etchant composed of 50 wt% of a sodium hydroxide solution at 85°C and using the same for performing clouding processing, a wafer was processed under the same condition as that in the example 1. [0032]

#### Comparative Example 3

Other than keeping the alkali etchant composed of 50 wt% of a sodium hydroxide solution at 80°C and using the same for performing clouding processing, a wafer was processed under the same condition as that in the example 1. [0033]

## Comparative Example 4

Other than keeping the alkali etchant composed of 40 wt% of a sodium hydroxide solution at 90°C and using the same for performing clouding processing in the example 1, a wafer was processed under the same condition as that in the example 1. [0034]

#### Comparative Example 5

Other than keeping the alkali etchant composed of 40 wt% of a sodium hydroxide solution at 85°C and using the same for performing clouding processing in the example 1, a wafer was processed under the same condition as that in the example 1. [0035]

## Comparative Example 6

Other than keeping the alkali etchant composed of 40 wt% of a sodium hydroxide solution at 80°C and using the same for performing clouding processing in the example 1, a wafer was processed under the same condition as that in the example 1. [0036]

## Comparative Example 7

Other than keeping the alkali etchant composed of 55 wt% of a sodium hydroxide solution at 80°C and using the same for performing clouding processing, a wafer was processed under the same condition as that in the example 1. [0037]

## [Gloss Level Lowering Test]

Measurement was made respectively on the wafers obtained in the examples 1 to 8 and comparative examples 1 to 7 as to a gloss level before being subjected to the clouding processing and a gloss level after the clouding processing by a gloss level meter (made by NIPPON DENSHOKU Co., Ltd.) based on the standard of gloss 60°, and the lowering rate (%) was also calculated. Also, front and back of the wafers were observed with eyes to evaluate whether the front and back can be identified or not. Wafers able to be identified were determined to be "o" and wafers unable to be identified were determined to be "o" and wafers unable to be identified were determined to be "x".

The results are shown in Table 1, FIG. 2 and FIG. 3. FIG. 2 is a graph showing whether front and back can be identified or not in combinations of weight concentration of the alkali etchant and the etching (clouding processing) temperature: wherein a "o" mark in the graph indicates a point that identification is possible, while a "×" mark indicates a point that identification is not possible. Also, a hatched field in the figure indicates a range that identification is possible. FIG. 3 is a graph showing a gloss level (%) with respect to weight concentration (wt%) of the alkali etchant.

[Table 1]				
	Weight	Clouding	Lowering Rate of	Capability of
	Concentration	Processing	Gloss Level	Identifying Front
	of Sodium	Temperature	Before and After	and Back
	Hydroxide	(°C)	Clouding	·
	(wt%)		Processing	
Example 1	70	90	81	0
Example 2	70	85	70	0

	·			
Example 3	70	80	55	0
Example 4	60	90	70	0
Example 5	60	85	55	0
Example 6	60	80	40	0
Example 7	55	90	50	0
Example 8	55	85	40	0
Comparative Example 1	50	90	15	×
Comparative Example 2	50	85	5	×
Comparative Example 3	50	80	0	×
Comparative Example 4	40	90	0	×
Comparative Example 5	40	85	0	×
Comparative Example 6	40	80	0 .	×
Comparative Example 7	55	80	31	×

[0039]

From the results of the examples 1 to 8 and comparative examples 1 to 7, a lowering rate of the gloss level has to be at least 40% or so for enabling to identify front and back of the mirror finished wafer with eyes, but it was confirmed that identifying of front and back of the mirror finished wafer with eyes becomes possible when the weight concentration of the alkali etchant is 60 wt% to 70 wt% and the etching temperature is 80°C to 90°C. Also, it was confirmed that when the weight concentration of the alkali etchant was 55 wt%, identifying of front and back of the mirror finished wafer with eyes becomes possible if the etching temperature is 85°C to 90°C. Accordingly, it is inferred that a slope has a relation of a minus linear function in a range that the etching temperature is 80 to 85°C when the weight concentration of the alkali etchant is 55 to 60 wt% as shown in FIG. 2.

[0040]

## Example 9

While keeping 51 wt% of a sodium hydroxide solution at 80°C, sodium hydroxide flakes having a purity of 99% were added thereto, so that an alkali etchant composed of a sodium hydroxide solution having weight concentration of 70 wt% was fabricated. In the alkali etchant kept at 80°C, one surface of a both-side mirror finished silicon wafer subjected to the processing in the steps S1 to S5 shown in FIG. 1 was immersed until an etching depth (allowance) reaches 10µm. The wafers, wherein one surface was subjected to clouding processing as above, were subjected to pure water washing, neutralizing processing, pure water washing and drying in respective steps of the steps S7 to S10 shown in FIG. 1. As a neutralizing agent in the step S8, a fluorinated acid solution in weight concentration of 10 wt% added with 10ppm of ozone was used and the processing was performed at a room temperature for 5 minutes.

[0041]

## Example 10

Other than changing an etching depth by the alkali etchant to 20µm in the example 9, a wafer was processed under the same condition as that in the example 9. [0042]

## Example 11

Other than changing an etching depth by the alkali etchant to  $30\mu m$  in the example 9, a wafer was processed under the same condition as that in the example 9. [0043]

#### Example 12

Other than changing an etching depth by the alkali etchant to  $40\mu m$  in the example 9, a wafer was processed under the same condition as that in the example 9. [0044]

#### Comparative Example 8

Other than using an alkali etchant composed of 50wt% of sodium hydroxide solution in the example 9, a wafer was processed under the same condition as that in the example 9.

[0045]

#### Comparative Example 9

Other than using an alkali etchant composed of 50wt% of sodium hydroxide solution in the example 10, a wafer was processed under the same condition as that in the example 10.

[0046]

## Comparative Example 10

Other than using an alkali etchant composed of 50wt% of a sodium hydroxide solution in the example 11, a wafer was processed under the same condition as that in the example 11.

[0047]

# Comparative Example 11

Other than using an alkali etchant composed of 50wt% of a sodium hydroxide solution in the example 12, a wafer was processed under the same condition as that in the example 12.

[0048]

## Confirmation Test of Global Flatness (GBIR)

Global flatness level GBIR(TTV) of a wafer before etching (clouding processing) and GBIR after the etching were respectively measured and a change rate thereof was also calculated. A thickness/flatness measurement apparatus (made by Japan ADE Ltd.) having a capacitance type distance sensor was used for measuring flatness level GBIR. Also, the site flatness SFQR and nano-topography (a difference (nm) of the maximum value and minimum value of a height in 2mm square) were measured.

	Etching	GBIR	GBIR	Change	Change	SFQR	Nano-topography	
	Depth	Before	After	Before	Rate of	after	After	Etching
	(µm)	Etching	Etching	and	GBIR	Etching	(nm)	
		(µm)	(µm)	After	(%)	(µm)		
				Etching				
				ΔGBIR				
				(µm)				
Example 9	10	0.65	0.70	0.05	0.5	0.065	15	
Example 10	20	0.70	1.00	0.30	1.5	0.150	30	
Example 11	30	0.60	1.50	0.90	3.0	0.205	>100	
Example 12.	40 ,	0.75	2.00	1.25	3.1	0.350	>100	
Comparative	10	0.60	0.95	0.35	3.5	0.175	50	

0.65

1.20

1.70

[0049]

Example 8
Comparative

Example 9
Comparative

Example 10

Comparative

Example 11

20

30

40

0.55

0.70

0.80

1.20

1.90

2.50

[Table 2]

From the results of the examples 9 to 12 and comparative examples 8 to 12, it was confirmed that a change rate of the global flatness level GBIR can be suppressed to about 3% even when the etching depth is 30 to 40µm if the weight concentration of the alkali etchant is 70 wt%. Also, the examples 9 to 12 exhibited more preferable values in the site flatness SFQR and nano-topography comparing with those in the comparative examples 8 to 11.

3.3

4.0

4.3

0.355

0.575

0.700

>100

>100

>100

[0050]

Note that the embodiments explained above are described to facilitate understanding of the present invention and is not to limit the present invention. Accordingly, respective elements disclosed in the above embodiments include all design modifications and equivalents belonging to the technical scope of the present invention.

# <BRIEF DESCRIPTION OF DRAWINGS>

[0051]

[FIG. 1] (A) is a view of a procedure showing a production method of a semiconductor wafer according to an embodiment of the present invention, (B) is a view of a procedure of a key part showing a production method of a semiconductor wafer according to another embodiment.

[FIG. 2] A graph showing a capability of identifying front and back in combinations of weight concentration of an alkali etchant and etching (clouding processing) temperature. [FIG. 3] A graph showing a gloss level (%) with respect to weight concentration (wt%) of alkali etchant.

<Name of Document> ABSTRACT

<Abstract>

# <A PROBREM TO BE SOLVED>

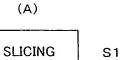
Providing an etchant capable of suppressing deterioration of a global flatness level and sufficiently lowering a gloss level of a wafer, and a production method of a semiconductor wafer.

# <MEANS FOR SOLVING THE PROBLEM>

An alkali etchant for controlling surface roughness of a semiconductor wafer, which is a sodium hydroxide solution having a weight concentration of 55 wt% to 70 wt%.

<SELECTED FIGURE> FIG. 1

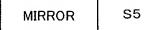












**ETCHING** 

(CLOUDING AND





NEUTRALIZING

(FLUORINATED

OZONE

SPRAYING +

**ETCHING** 

(CLOUDING AND

¦S6

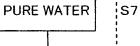
**S**7

S8'

S9

S10'

(B)

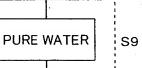


S6

S8

S10









DRYING

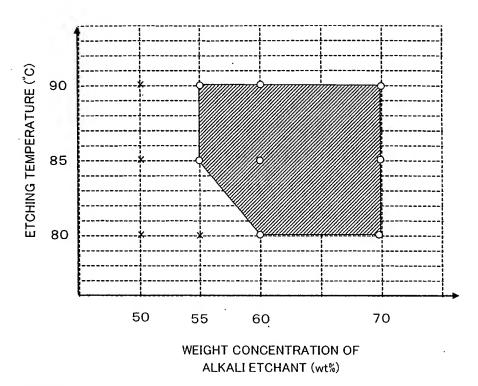
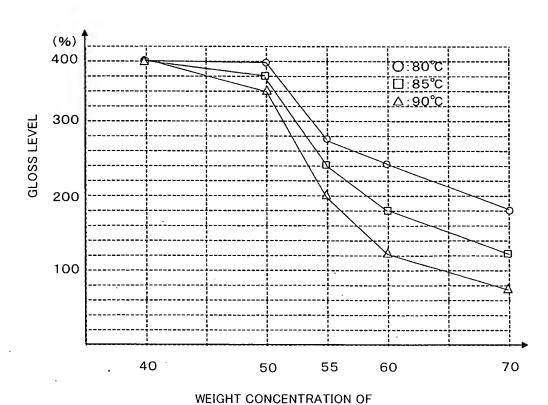


FIG. 3



ALKALI ETCHANT (wt%)